

DECREASING PINHOLE DEFECT FORMATION PROBABILITY ON COBALT FELDSPAR GLAZES FOR PORCELAIN PRODUCTION

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Translated from *Steklo i Keramika*, No. 3, pp. 16 – 17, March, 2011.

Pegmatite from the Chupin deposit with mica impurities which is used for the production of glaze for porcelain can be responsible for the formation of pinhole defects. It has been established that adding calcinated kaolin to cobalt feldspar glaze decreases the formation probability of this defect.

Key words: feldspar glazes, porcelain, cobalt oxide, calcinated kaolin, glaze defects, pegmatite, mica.

The quality of the glaze layer determines not only the application but also the decorative-aesthetic properties of porcelain articles. The surface state of glazed porcelain affects the character of light reflection from it. The color perception of objects which have the same color but a different luster is not the same [1].

The degree of brightness largely depends on the surface state of the glaze. A defect such as a pinhole degrades the decorative properties (loss of brightness) and service properties of glazed porcelain (the article becomes dirty more easily). One of the main reasons for the appearance of pinholes on feldspar porcelain glaze after glaze firing is the presence in the raw materials of mica impurities [2]. Mica dehydration occurs at quite high temperatures 800 – 1200°C. As a result of reactions, gases capable of forming quite large bubbles in the glaze layer are released, which results in the appearance of pinholes on the surface.

Russian enterprises producing porcelain traditionally use as the main quartz-feldspar raw material pegmatite from the Chupinskoe deposit in Karelia. According to the GOST 7030–75 requirements KNShM-0.2-2 pegmatite for fine ceramic (porcelain, glazed earthenware, electrotechnical ceramic) must have the following characteristics: (CaO + MgO) — no more than 2%³; (K₂O + Na₂O) — not less than 8%; free quartz — no more than 30%; potassium modulus K₂O/Na₂O — not less than 2; number of mica flakes — no more than 2 flakes per 100 grains of pegmatite.

Deep blue feldspar (cobalt) glazes, which are obtained using cobalt oxide, are found to be most sensitive to the formation of pinholes. To obtain intense color they are depo-

sited in a thicker layer on the intermediate product (the working density of the suspension of the cobalt glaze is 1.31 – 1.32 g/cm³), which increases the probability for the appearance of pinholes. After glaze firing a 200 – 250 μm thick glassy layer for cobalt glazes and 100 – 120 μm thick for colorless glazes are formed on the porcelain.

The glaze layer is largely represented by glass. It can also contain gas bubbles-pores, unreacted grains of quartz, and crystal embryos. Just as glass, glaze does not have a definite softening point; this point is characterized by the existence of a temperature interval between softening onset (lower limit of meltability) and complete melting (upper limit of meltability).

It is believed that to decrease the probability of pinhole formation the lower limit of meltability must be higher than the temperature at which all processes occurring in the glaze and porcelain and associated with gas-release have gone to completion. To increase the refractoriness of the glazes Al₂O₃, SiO₂, and ZrO₂ can be introduced into the mix composition [3].

To avoid pinhole defects in porcelain glazes based on Chupinskoe pegmatite from the technological group “Keramika Gzheli” JSC a decision was made to introduce calcinated kaolin into the mix. With respect to its mineral composition this material is dehydrated kaolin and contains the following: 43 – 47% Al₂O₃, 50 – 54% SiO₂, and < 0.5% Fe₂O₃. This material was chosen on the basis of two factors: completion in the material of reactions accompanied by gas release and the content of a substantial amount of Al₂O₃ and SiO₂, which raise the melting temperature of glassy coatings.

A colorless glaze was used as a the base glaze for porcelain with the recommended firing temperature 1320°C and the following chemical composition (%): 69.59 SiO₂; 13.96 Al₂O₃;

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³ Here and below content by weight.

TABLE 1. Properties of the Glaze with Introduction of Calcinated Kaolin Additions

Glaze sample	Molecular formula	Computed CLTE, 10^{-6} K^{-1}	Computed melting temperature, $^{\circ}\text{C}$
No additive	0.248R ₂ O	6.5	1326.4
	0.752RO		
	0.003Fe ₂ O ₃		
	0.006TiO ₂		
	0.419Al ₂ O ₃		
With additive	3.451SiO ₂	6.4	1334.2
	0.247R ₂ O		
	0.753RO		
	0.003Fe ₂ O ₃		
	0.006TiO ₂		
	0.421Al ₂ O ₃		
	3.465SiO ₂		

0.19 Fe₂O₃; 6.20 CaO; 3.48 MgO; 1.99 Na₂O; 4.46 K₂O; and, 0.13 TiO₂. The addition of 1.8 – 2% calcinated kaolin (this amount was determined experimentally) was made during combined grinding. Finely dispersed cobalt oxide was added in amounts 3 – 4% to obtain a glaze with cobalt-blue color.

Calculations of the molecular formula (see Table 1), the CLTE, and the melting temperature by Langersdorf's method [4] for the glaze base showed that the introduction of calcinated kaolin as an additive resulted in the following:

– an increase in the molecular formula of the Al₂O₃ and SiO₂ fraction;

– a negligible decrease of the CLTE;
 – an increase of the computed melting temperature of the glaze.

It was established in practice that a small shift of the meltability intervals toward higher temperature improves the surface state of cobalt glaze but does not degrade the pouring quality. Adding calcinated kaolin decreases the number of large pinholes in the glaze considerably. An increase of the brightness of the glaze with intense blue color preserved is noticeably visually.

Calcinated kaolin is an easily accessible, nontoxic, and inexpensive material and can be an effective means for decreasing the probability of formation of pinhole defects on the surface of glaze on articles made of fine ceramics at enterprises using domestic quartz-feldspar raw material.

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